Lecture 14

<u>The ground state of Helium</u>

Our initial trial function was:

$$\psi_0 = \frac{8}{\pi a^3}\, e^{-\overset{Z}{2}(r_1+r_2)/a}$$

Now, we take
$$\boxed{\psi_0 = \frac{Z^3}{\pi a^3}\, e^{-Z(r_1+r_2)/a}}$$

and take Z to be a parameter. We re-write the Hamiltonian as

our ψ_0 is eigenfunction of this Hamiltonian

$$H = \underbrace{\boxed{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)}}_{H_0}$$

$$+ \underbrace{\frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2}\right)}_{H_1} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\bar{r}_1 - \bar{r}_2|}}_{V_{ee}}$$

Note, that we did not change our Hamiltonian (we are not allowed to do that in the variational method). We just added and subtracted

$$\frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right).$$

We now calculate the expectation value

$$\langle\psi_0|H|\psi_0\rangle = \langle\psi_0|H_0|\psi_0\rangle + \langle\psi_0|H_1|\psi_0\rangle + \langle\psi_0|V_{ee}|\psi_0\rangle.$$

with our "new" trial function

$$\psi_0 = \frac{Z^3}{\pi a^3}\, e^{-Z(r_1+r_2)/a} \equiv \underbrace{\psi_{100}(\bar{r}_1)\,\psi_{100}(\bar{r}_2)}_{\text{with charge } Z}$$

$$\langle \psi_0 | H_0 | \psi_0 \rangle = \langle \psi_0 | E_0 \psi_0 \rangle = 2E_1 \frac{Z^2}{1^2} \langle \psi_0 | \psi_0 \rangle^{\nearrow 1}$$

$$= 2E_1 Z^2$$

Note: if Z=2 $\langle H_0 \rangle = 2E_1 \cdot 2^2 = 8E_1$ as before.

$$\langle \psi_0 | H_1 | \psi_0 \rangle = \langle \psi_0 | \frac{e^2}{4\pi\epsilon_0} \frac{Z-2}{r_1} | \psi_0 \rangle + \langle \psi_0 | \frac{e^2}{4\pi\epsilon_0} \frac{Z-2}{r_2} | \psi_0 \rangle$$

$$= \frac{e^2}{4\pi\epsilon_0}(Z-2) \iint \psi^*_{100}(\vec{r}_1)\psi^*_{100}(\vec{r}_2) \frac{1}{r_1} \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)\, d^3\vec{r}_1\, d^3\vec{r}_2$$

$$+ \frac{e^2}{4\pi\epsilon_0}(Z-2) \iint \psi^*_{100}(\vec{r}_1)\psi^*_{100}(\vec{r}_2) \frac{1}{r_2} \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)\, d^3\vec{r}_1\, d^3\vec{r}_2$$

$$= \frac{e^2}{4\pi\epsilon_0}(Z-2) \Big\{ \underbrace{\int \psi^*_{100}(\vec{r}_1) \frac{1}{r_1} \psi_{100}(\vec{r}_1)\, d^3\vec{r}_1}_{\langle \psi_{1s} | \frac{1}{r} | \psi_{1s} \rangle \equiv \langle \frac{1}{r} \rangle_{1s}} \underbrace{\int \psi^*_{100}(\vec{r}_2)\psi_{100}(\vec{r}_2)\, d^3\vec{r}_2}_{\substack{1 \\ \text{(normalized)}}}$$

$$+ \underbrace{\int \psi^*_{100}(\vec{r}_1)\psi_{100}(\vec{r}_1)\, d^3\vec{r}_1}_{=1} \underbrace{\int \psi^*_{100}(\vec{r}_2) \frac{1}{r_2} \psi^*_{100}(\vec{r}_2)\, d^3\vec{r}_2}_{\langle \frac{1}{r} \rangle_{1s}} \Big\}$$

$$= 2\frac{e^2}{4\pi\epsilon_0}(Z-2)\left\langle \frac{1}{r} \right\rangle_{1s}$$

We need to calculate $\left\langle \frac{1}{r} \right\rangle_{1s} \equiv \langle \psi_{1s} | \frac{1}{r} | \psi_{1s} \rangle$

$$\psi_{1s} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0}$$

where a_0 is the Bohr radius $a_0 \equiv \frac{4\pi\epsilon_0}{me^2}\hbar^2$

Note: $a = \frac{4\pi\epsilon_0}{me^2 Z}\hbar^2 = \frac{a_0}{Z}$ since $e^2 \to e^2 Z$ for H-like atoms.

$$\left\langle \frac{1}{r} \right\rangle_{1s} = \frac{Z^3}{\pi a_0^3} \int_0^\infty e^{-2Zr/a_0} \frac{1}{r} r^2 \, dr \underbrace{\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$= \frac{4\pi Z^3}{\pi a_0^3} \underbrace{\int_0^\infty e^{-2Zr/a_0} r \, dr}_{\frac{a_0^2}{4Z^2}} = \frac{\cancel{4}\cancel{\pi} Z^{\cancel{3}}}{\cancel{\pi} a_0^{\cancel{3}}} \frac{\cancel{a_0}}{\cancel{4}\cancel{Z^2}} = \frac{Z}{a_0}$$

We already calculated the third term:

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) \quad \text{(previous result)}$$

For our new trial function, $a \to 2a_0/Z$

$$\langle V_{ee} \rangle = \frac{5}{4a_0} \frac{Z}{2} \frac{e^2}{4\pi\epsilon_0} = \frac{5Z}{8a_0} \frac{e^2}{4\pi\epsilon_0}$$

Putting it all together, we get

$$\langle H \rangle = 2E_1 Z^2 + 2(Z-2)Z \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} + \frac{5Z}{8} \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$$

For convenience, let's express all terms via E_1:

$$E_1 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$$

$$a_0 = \frac{4\pi\epsilon_0}{me^2} \hbar^2 = \left(\frac{e^2}{4\pi\epsilon_0} \right)^{-1} \frac{\hbar^2}{m} \Rightarrow$$

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} = \frac{e^2}{4\pi\epsilon_0} \frac{e^2}{4\pi\epsilon_0} \frac{m}{\hbar^2} = -2E_1$$

$$\langle H \rangle = 2E_1 Z^2 - 4E_1 (Z-2) Z - \frac{5}{4} Z E_1$$

$$= E_1 \left(2Z^2 - 4Z^2 + 8Z - \frac{5}{4} Z \right) = E_1 \left(-2Z^2 + \frac{27}{4} Z \right)$$

Therefore, for any Z

$$\langle H \rangle \geqslant E_{gs}$$

We yet the lowest upper bound when $\langle H \rangle$ is minimized, i.e. $\frac{d\langle H \rangle}{dZ} = 0$.

Class exercise: minimize $\langle H \rangle$. Find Z and get the lowest upper bound for E_{gs} (i.e. a number in eV).

$$\frac{d}{dZ}\langle H \rangle = \left(-4Z + \frac{27}{4} \right) E_1 = 0$$

$$Z = \frac{27}{16} = 1.69$$

$$\langle H \rangle = E_1 \left(-2Z^2 + \frac{27}{4} Z \right) = -13.6 \left(-2 \cdot (1.69)^2 + \frac{27}{4} 1.69 \right)$$

$$\langle H \rangle = -77.5 \text{ eV}$$

Even closer to the experimental value -79.0 eV!

Summary: variational method

The variational principle let you get an **upper bound** for the ground state energy when you can not directly solve the Schrödinger's equation.

How does it work?

(1) Pick any normalized function ψ .

(2) The ground state energy E_{gs} is

$$\boxed{E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle}$$

3) Some choices of the trial function ψ will get your E_{gs} that is close to actual value.

If you picked a function with a parameter, minimize the resulting expression for $\langle H \rangle$. Substitute resulting value of the parameter into $\langle H \rangle$ to get lowest upper bound on E_{gs}.

The WKB approximation

WKB: Wentzel, Kramers, Brillouin

This method allows to obtain approximate solutions to the time-independent Schrödinger equation in one dimension and is particularly useful in calculating tunneling rates through potential barriers and bound state energies.

Main idea:

(1) If **potential V is constant** and energy E of the particle is E>V, then the particle wave function has the form

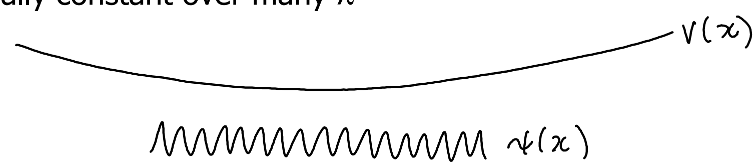
particle is travelling to the right

$$\psi(x) = A e^{\pm ikx}, \quad k = \sqrt{2m(E-V)}/\hbar$$

particle is travelling to the left

General solution is a linear superposition of the two.
The wave function is oscillatory with a fixed wavelength $\lambda = 2\pi/k$
and fixed amplitude A.

(2) If V (x) is not constant, but varies slow in comparison with the wavelength λ in a way that it is essentially constant over many λ



then the wave function is practically sinusoidal, but wavelength and amplitude slowly change with x.

Summary: rapid oscillations are modulated by gradual changes in amplitude and wavelength.

If E<V and V is constant, then wave function is

$$\psi(x) = A e^{\pm \kappa x} \qquad \kappa = \sqrt{2m(V-E)}/\hbar$$

If V is not constant but varies slowly with comparison to $1/\kappa$, then the wave function is practically exponential but A and κ are slowly-varying functions of x.

Problem: turning points when V ≈ E. Then, V(x) is not slowly varying with comparison to λ or $1/\kappa$ since λ $(1/\kappa) \to \infty$.

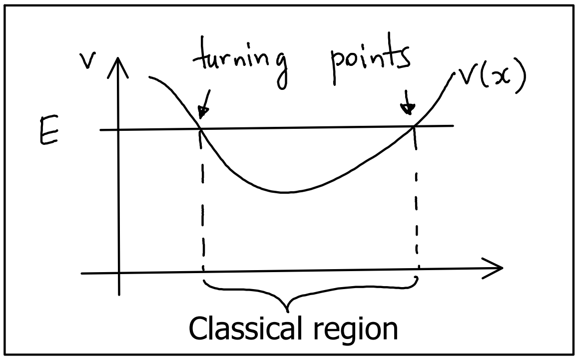
The "classical" region

Let's now solve the Schrödinger equation using WKB approximation.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$(2) \qquad \frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \quad , \quad p(x) = \sqrt{2m(E-V(x))}$$

We assume for now that E>V (x) and p is real.
ψ is some complex function, and therefore can be expressed as



phase

$$\psi(x) = A(x)\, e^{i\phi(x)} \qquad (1)$$

amplipude

Class exercise: plug this expression (1) back into (2) and separate real and imaginary parts into two equations.

$$\frac{d\psi}{dx} = \frac{d}{dx}(A e^{i\phi}) = A' e^{i\phi} + i\phi' A e^{i\phi} = (A' + i\phi' A)\, e^{i\phi}$$

$$\frac{d^2\psi}{dx^2} = A'' e^{i\phi} + i\phi' A' e^{i\phi} + i\phi'' A e^{i\phi} + i\phi' A' e^{i\phi}$$

$$+ i\phi' A (i\phi') e^{i\phi} = \left(A'' + 2i\phi' A' + iA\phi'' - A(\phi')^2\right) e^{i\phi}$$

$$\boxed{A'' + \underline{2i\phi' A'} + \underline{iA\phi''} - A\phi'^2 = -\frac{p^2}{\hbar^2}A}$$

$$\boxed{A'' - A\phi'^2 = -\frac{p^2}{\hbar^2}A} \qquad (3)$$

$$\boxed{2\phi' A' + A\phi'' = 0} \qquad (4)$$

We solve Eq.(4) first:

$$2A'\phi' + A\phi'' = 0$$

$$(A^2\phi')' = 0 \quad (\text{check: } 2AA'\phi' + A^2\phi'' = 0)$$

$$A^2\phi' = \underset{\uparrow \text{ some real constant}}{c^2}$$

$$\boxed{A = \frac{c}{\sqrt{\phi'}}}$$

To solve Eq.(4), we assume that amplitude A varies slowly, so term A" is negligible.

$$\underset{\uparrow \text{ drop this term}}{A''} - A(\phi')^2 = -\frac{p^2}{\hbar^2}A$$

$$(\phi')^2 = \frac{p^2}{\hbar^2} \Rightarrow \frac{d\phi}{dx} = \pm\frac{p}{\hbar}$$

$$\phi(x) = \pm\frac{1}{\hbar}\int p(x)\,dx$$

$$\boxed{\psi(x) \cong \frac{c}{\sqrt{p(x)}} e^{\pm\frac{i}{\hbar}\int p(x)\,dx}} \qquad p(x) = \sqrt{2m(E - V(x))}$$

General solution is the combination of these two.